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[54] Title of Invention: Refining method for toluene containing nitrogenous impurities

[57] Abstract

The present invention discloses a refining method for toluene containing nitrogenous impurities, wherein toluene containing nitrogenous impurities comes into contact with a sulphonic acid cation exchange resin layer under conditions of room temperature to 80°C and a linear velocity of less than 10.0 m/hour to remove the nitrogenous impurities therein. This method has the advantages of good results, simple operation and low cost.

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Claims

1. A refining method for toluene containing nitrogenous impurities, characterised in that toluene containing nitrogenous impurities comes into contact with a cation exchange resin layer under conditions of room temperature to 80°C and a linear velocity of less than 10.0 m/hour.
2. Method according to Claim 1, characterised in that toluene containing nitrogenous impurities comes into contact with a cation exchange resin layer at a temperature of 40-60°C and a linear velocity of 4-6 m.
3. Method according to Claim 1, characterised in that the said cation exchange resin is a sulphonic acid cation exchange resin.
4. Method according to Claim 3, characterised in that the said sulphonic acid cation exchange resin is a styrene system ion exchange resin.
5. Method according to Claim 4, characterised in that the said styrene system ion exchange resin is a large pore ion exchange resin.
6. Method according to Claim 1, characterised in that before the said cation exchange resin is used, it must be changed from a storage type to a hydrogen type, the treatment steps being: the storage type cation exchange resin is soaked in deionised water at room temperature for more than 24 hours, after which a solution of hydrochloric acid of 4-5 times the volume of the ion exchange resin and with a concentration of 3-4 (weight)% flows through the ion exchange resin for 1-2 hours, followed by flushing out the resin with deionised water until the pH value of the washings is 6-7.

Description

Refining Method for Toluene Containing Nitrogenous Impurities

The present invention relates to a refining method for toluene containing nitrogenous impurities.

The toluene product currently obtained from the aromatic hydrocarbon extraction process using formylmorpholine as the solvent contains such organic nitrogenous impurities as morpholine and formylmorpholine giving a nitrogen content calculated at 10 $\mu\text{g/g}$, and such a high nitrogenous impurity content will cause poisoning of the downstream process catalyst. It is therefore necessary to remove them from the toluene by means of a refining method, so that the refined toluene will have a nitrogen content reduced to below 1 $\mu\text{g/g}$.

Refining of toluene containing nitrogenous impurities is currently universally by the two methods of aqueous washing and belozem refining.

Aqueous washing requires the consumption of large quantities of water resources and not only results in high energy consumption, but the nitrogenous effluent produced from the aqueous washing also requires further treatment.

The belozem refining method is conducted with staged temperature rises, and the belozem requires replacement every 3-6 months. This not only increases the operational complexity for operating personnel as well as the size of the labour force, but the large quantity of replaced waste belozem also poses "Three Wastes" treatment problems.

The objective of the present invention is to provide a new method for refining toluene containing nitrogenous impurities, featuring simple operation, little contamination and low cost.

The refining method provided by this invention involves toluene containing nitrogenous impurities coming into contact with a sulphonic acid cation exchange resin layer under conditions of room temperature to 80°C and a linear velocity of less than 10.0 m/hour.

The said refining conditions in this invention are preferably temperature 40-60°C and linear velocity 4-6 m/hour.

The said cation exchange resin of this invention is a sulphonic acid cation exchange resin containing a sulphonic acid group ($-\text{SO}_3\text{H}$), and is preferably a styrene system - sulphonic acid ion exchange resin, and better still is a large pore styrene system - sulphonic acid ion exchange resin.

Commercially available cation exchange resins are generally of the storage type, and before use they require pre-treatment to change them from storage type to hydrogen type, the pre-treatment steps being as follows:

The storage type cation exchange resin is soaked in deionised water at room temperature for more than 24 hours, after which a solution of hydrochloric acid of 4-5 times the volume of the ion exchange resin and with a concentration of 3-4 (weight)% flows through the ion exchange resin for 1-2 hours, followed by flushing out the resin with deionised water until the pH value of the washings is 6-7.

After loss of activity of the said cation exchange resin through use, it can continue to be used after regeneration, the regeneration method being the same as the resin pre-treatment method.

The method of this invention has the following advantages:

- (1) The results are good, and the organic nitrogen content in the toluene can be reduced from 50 $\mu\text{g/g}$ to below 1 $\mu\text{g/g}$.
- (2) Operation is simple and convenient.
- (3) The cation exchange resin can be repeatedly regenerated and used multiple times, thus lowering refining costs.

This invention is further described below by means of practical examples, but the scope of this invention is not limited by these practical examples.

In the practical examples, the nitrogenous impurity content in the toluene samples was measured according to the measurement method for residual nitrogen measurement in liquid petroleum alkanes in Petrochemical Industry Standard SH/T0657-1998 of the People's Republic of China.

Practical Examples 1-7

The following practical examples describe the process for treating toluene samples containing morpholine impurity by the method of this invention.

30 g of large pore sulphonic acid cation exchange resin (product of the Chemical Engineering Works of Nankai University, product number D001) was soaked in deionised water for 30 hours and was then packed in a glass column, and four times the volume of 4 (weight)% of hydrochloric acid solution was passed through the resin for one hour to convert it to a hydrogen type, and it was then flushed with deionised water until the pH value of the washings was 6.0-7.0, when the flushing was stopped, and the water was removed with gaseous nitrogen.

Toluene containing morpholine impurity with a nitrogen content calculated at 53 $\mu\text{g/g}$ was passed through the ion exchange column under various conditions. See Table 1 for the treatment conditions and the nitrogen content in the toluene following treatment.

Practical Examples 8-14

The following practical examples describe the process for treating toluene samples containing formylmorpholine impurity by the method of this invention.

30 g of large pore sulphonic acid cation exchange resin (product of the Chemical Engineering Works of Nankai university, product number D001) was soaked in deionised water for 25 hours and was then packed in a glass column, and four times the volume of 4 (weight)% of hydrochloric acid solution was passed through the resin for one hour to convert it to a hydrogen type, and it was then flushed with deionised water until the pH value of the washings was 6.0-7.0, when the flushing was stopped, and the water was removed with gaseous nitrogen.

Toluene containing formylmorpholine impurity with a nitrogen content calculated at 37 $\mu\text{g/g}$ was passed through the ion exchange column under various conditions. See Table 2 for the treatment conditions and the nitrogen content in the toluene following treatment.

Table 1

Practical Example	Treatment Conditions	Nitrogen Content ($\mu\text{g/g}$)
1	Room temp, 2 m/hour	0.33
2	40°C, 4 m/hour	0.43
3	40°C, 6 m/hour	0.62
4	40°C, 8 m/hour	0.82
5	50°C, 6 m/hour	0.52
6	60°C, 6 m/hour	0.34
7	80°C, 6 m/hour	0.31

Table 2

Practical Example	Treatment Conditions	Nitrogen Content
8	Room temp, 2 m/hour	0.24
9	40°C, 4 m/hour	0.33
10	40°C, 6 m/hour	0.48
11	40°C, 8 m/hour	0.64
12	50°C, 6 m/hour	0.38
13	60°C, 6 m/hour	0.35
14	80°C, 6 m/hour	0.30

Practical Examples 15-21

The following practical examples describe the process for treating toluene samples containing morpholine and formylmorpholine impurities by the method of this invention.

30 g of large pore sulphonic acid cation exchange resin (product of the Chemical Engineering Works of Nankai University, product number D001) was soaked in deionised water for 30 hours and was then packed in a glass column, and four times the volume of 4 (weight)% of hydrochloric acid solution was passed through the resin for one hour to convert it to a hydrogen type, and it was then flushed with deionised water until the pH value of the washings was 6.0-7.0, when the flushing was stopped, and the water was removed with gaseous nitrogen.

Toluene containing morpholine and formylmorpholine impurities with nitrogen contents calculated at 26 $\mu\text{g/g}$ and 19 $\mu\text{g/g}$ was passed through the ion exchange column under various conditions. See Table 3 for the treatment conditions and the nitrogen content in the toluene following treatment.

Table 3

Practical Example	Treatment Conditions	Nitrogen Content
15	Room temp, 2 m/hour	0.29
16	40°C, 4 m/hour	0.38
17	40°C, 6 m/hour	0.55
18	40°C, 8 m/hour	0.73
19	50°C, 6 m/hour	0.45
20	60°C, 6 m/hour	0.34
21	80°C, 6 m/hour	0.31

Practical Examples 22-28

These practical examples describe the refining results from using a gel type styrene system sulphonic-acid-based resin.

After treating 30 g of a cation exchange resin (product of the Chemical Engineering Works of Nankai University, product number 001x7) by the method in Practical Example 1, toluene

containing morpholine impurity with a nitrogen content calculated at 53 $\mu\text{g/g}$ was passed through the exchange column under various conditions. See Table 4 for the treatment conditions and post-treatment nitrogen content in the toluene.

Table 4

Practical Example	Treatment Conditions	Nitrogen Content $\mu\text{g/g}$
22	Room temp, 2 m/hour	0.37
23	40°C, 4 m/hour	0.48
24	40°C, 6 m/hour	0.67
25	40°C, 8 m/hour	0.90
26	50°C, 6 m/hour	0.61
27	60°C, 6 m/hour	0.52
28	80°C, 6 m/hour	0.42